

ISOBARIC ADSORPTION AND DESORPTION OF HYDROCARBONS FOR THE DETERMINATION OF A WIDE RANGE OF PORE ENERGY DISTRIBUTIONS

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INTRODUCTION

Several standard methodologies are employed to determine the adsorptive properties of activated carbon.¹ These methodologies have, as a common goal, the generation of isotherm data. The isotherm data collected, in concert with any of the methodologies, can be used to calculate pore radius distributions using the Kelvin Equation,² surface areas using B.E.T.³ and Langmuir Theories,⁴ spreading pressures from the Gibb's Equation,⁵ and adsorption potential distributions using Polanyi Theory.⁶

Gas phase isotherm data is typically collected by either of two methods.¹ In the first, the concentration of the adsorbate is varied while maintaining the temperature and total pressure of the system constant. This method is limited by difficulties in controlling both temperature and adsorbate concentration over the time period required to reach equilibrium. In the second method, the pressure of the adsorbate is varied while maintaining the temperature of the system constant. This method is limited mainly by the achievable system pressures and diffusional constraints.

Carbon capacities can also be measured by maintaining the adsorbate pressure at some constant value and varying the temperature to several known values.¹ Such isobaric data can easily be collected if the system pressure is selected at some convenient value such as atmospheric pressure. Using the undiluted adsorbate gas at atmospheric pressure, mass transfer is rapid, especially at high temperatures, and equilibrium is quickly achieved. The isobaric data can then be converted into the more useful isothermal result using Polanyi Adsorption Theory. Alternatively, the Dubinin-Radushkevich Equation⁷ can be used for the same purpose. In the following sections a method is presented which provides a fast, convenient means for collection of isobaric carbon adsorption data. The isobaric data is correlated with isothermal data using Polanyi Adsorption Theory.⁸

EXPERIMENTAL

System Description

Isobars were determined using a customized instrument fabricated by George Associates (Berkeley, Ca.). The instrument was able to attain temperatures of -150°C to 600°C with positive and negative temperature ramping capabilities.

Procedures

Isobars - All isobars were performed at atmospheric pressure. Gravimetric determinations were performed once the system had reached both thermal and mass equilibria as indicated by no more than a 0.1°C change in temperature over one minute and no more than a 0.2 mg weight change over the same period. Samples were conditioned at 250°C in nitrogen prior to the determinations. Pure methane or ethane was adsorbed onto the sample in a series of 10 individual steps which were accomplished by incrementally decreasing and holding the temperature at each of several levels. After completing the adsorptive process, the methane or ethane was desorbed in a similar manner by increasing the temperature step-wise to the starting value. The amount of adsorbate loading was calculated as the mass difference between the equilibrated and the conditioned sample after making corrections for buoyancy effects.

Isotherms - Ethane isotherms were determined using granular material that had been previously dried in air at 150°C for three hours. Isotherms were performed at $25.0 \pm 0.1^\circ\text{C}$ in a water bath. The adsorbate gas was passed through a copper heat exchanger prior to contacting the carbon which was contained in a glass u-tube in the water bath. Gas flow was maintained until the mass change of the sample was less than 5 mg over an eight-hour period.

Methane isotherms were performed by the volumetric expansion method. A known volume and pressure of methane was allowed to expand into a vessel containing the activated carbon under vacuum. The amount of methane adsorbed was determined from the change in pressure of the system taking into account the void volume of the vessel containing the activated carbon. Void volumes were determined using helium expansion. The system was thermostatted at $25.0 \pm 0.1^\circ\text{C}$. Samples were conditioned at 100°C under vacuum for 6 hours. No difference in adsorption capacity was observed when the samples were conditioned at 250°C.

RESULTS AND DISCUSSION

Methane and ethane were chosen as the adsorbate compounds. These molecules lack any significant dipole or induced dipole characteristics⁹ such that only van der Waals interactions with the carbon are important. Within the temperature bounds of the isobars, both methane and ethane are stable with the exclusion of oxygen and the avoidance of catalytic metals.

Isobars can be presented as a plot of adsorbate capacity versus adsorption energies by employing Polanyi Theory. Following Polanyi Theory, the energy of adsorption, ϵ , is equal to the work required to take a molecule from the bulk phase to the adsorbed phase according to the following relationship:

$$\epsilon = \int_{\text{Bulk}}^{\text{Ads}} \bar{V} dp = RT \ln \frac{f_s}{f} \quad (1)$$

where f_s is the saturation pressure fugacity of the adsorbate at temperature $T(^{\circ}\text{K})$, f is the vapor fugacity of the adsorbate, and R is the gas constant. For isotherms, T is held constant while f is varied either by changing the concentration of the component in a diluent stream or by varying the absolute pressure of the adsorbate. For isobars, the temperature of the adsorbate or probe gas is varied thereby changing the value of f_s .

f_s can be calculated at any temperature below the critical temperature by use of the Antoine Equation and Peng-Robinson EOS. Above the critical temperature, the following expression was used to calculate the saturation pressure:¹⁰

$$P_s = \left(\frac{T}{T_c} \right)^2 P_c \quad (2)$$

Adsorbed phase densities were calculated according to the following equations:^{11,12}

$$V_A = V_m e^{\Omega(\sigma - \tau_0)} \quad (3)$$

$$\Omega = \frac{\ln \left(\frac{b}{V_m} \right)}{T_c - T} \quad (4)$$

Where V_A and V_m are the adsorbed phase molar volume and molar volume of the adsorbate liquid at the normal boiling point temperature, respectively. b is the van der Waals volume.

The isobar adsorption and desorption loadings for a single adsorbate onto a specific carbon are plotted as a function of ϵ as shown in Figure 1. As can be seen, the data points define a smooth curve that is typical for all carbons examined to date. The regularity of these data can be easily described by fitting the data to a polynomial of seventh order or less. The curves which can be described by the adsorption and desorption polynomials, are essentially collinear. This result clearly shows that equilibrium conditions were established at each isobaric point. No adsorption-desorption hysteresis has, as yet, been observed for any activated carbon using this technique with methane or ethane as probe gases. The smooth isobaric curves illustrate why it is not necessary to collect large numbers of adsorption and desorption isobaric points or to collect isobaric points at corresponding temperatures. This not only simplifies the method for generation of the isobaric data but also provides a significant advantage over isothermal techniques where temperatures need to be accurately known and precisely controlled. For the case of the isobaric techniques, the carbon and adsorbate gas need only to be in thermal equilibrium at a precisely known temperature. The Dubinin-Radushkevich Equation provides an alternate means of describing the data. The form of this equation is the logarithm of the volume adsorbed versus the square of ϵ .^{7,13}

Correlation of Isobars with Isotherms

By use of Equation 1, ϵ values can be calculated from isotherm data as well as from isobar data. This provides a convenient way of reducing the data for comparative purposes. For example, Table 1 presents the ϵ values for each isotherm concentration as well as the temperature of the pure component isobar at equivalent ϵ values. Once the data have been reduced to a common scale, with reference to the ϵ -parameter, comparisons can be made between the techniques. A graphical representation of this comparison is given in Figure 2 for a single carbon. As can be seen, the isobar and isotherm data are essentially interchangeable at the individual ϵ -values. Therefore, this technique provides a convenient method to generate simple isotherms from isobaric data. Table 1 also illustrates the advantage of the isobar technique to generate adsorbate loadings at various pore energies. In the case of ethane, an increase in temperature from 25°C to 220°C is equivalent to reducing the concentration or partial pressure of the adsorbate by two orders of magnitude. The operating temperature range for isobar determinations for ethane from -76 to 250°C is equivalent to greater than a three order of magnitude change in isotherm concentration. When utilizing the isotherm technique, this reduction in concentration to the resulting low adsorbate concentration levels requires the consumption of large quantities of adsorbate gas and extended time periods in making isotherm determinations.

The average relative standard deviation for the isobaric technique was 8.7% versus 4.3% for the isotherms. A statistical comparison of the variances of the isotherms versus isobars was made using the F-test at the 0.05 statistical level. The variance of the methane and ethane isobars versus the respective isotherms was found to be equal. This analysis was based upon the use of three replicates for both of the experimental techniques for the six carbons investigated.

Table 1 presents a summary of the average errors between the isotherms and isobars. No systematic errors were observed between the two techniques. Differences were examined using the student's T-test at the 0.05 statistical level. The methods were found to produce equivalent results over the adsorption energy range studied.

CONCLUSIONS

A method has been demonstrated that permits the generation of isotherm data from isobaric data. The method is rapid and generates estimates of isotherms with an accuracy and precision comparable to those generated by traditional means. The principal advantage of the isobar procedure

is that equilibration is rapid as higher temperatures and neat adsorbates are used. A span of greater than three orders of magnitude in f_i/f can be attained by varying the temperature of the system by several hundred degrees. The time required for the analysis is typically about four hours, whereas the time to perform isotherms which span the same energy region would require days-to-weeks to gain an equivalent amount of information.

Future directions in our research program will include the correlation of the isobar data with isotherm results from other classes of compounds. The achievement of such correlations will greatly enhance the utility of a variety of carbon performance predictive models. The models that would benefit most from this method are those that depend upon the determination of single component isotherms over a wide adsorbate concentration range for a specific carbon.

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Table 1
Equivalence in Adsorption Energies for Isotherms and Isobars

	Methane			Ethane		
ϵ (Kcal/mole)	1.83	2.14	2.90	1.95	3.31	4.68
Temperature of Pure Component Isobar ($^{\circ}\text{C}$)	-40.7	-15.1	28.5	25.0	103.7	222.2
Isotherm Partial Pressure of Adsorbate (mm Hg)	5500	3137	782	745	74.5	7.5
Average Error Between Isotherms and Isobars (%)	1.6	-2.2	5.5	-3.3	-5.1	11.9

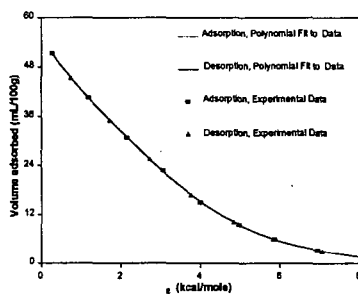


Figure 1
Adsorption and Desorption Isotherms
Ethane Adsorbed on Xtrisorb 700 Carbon

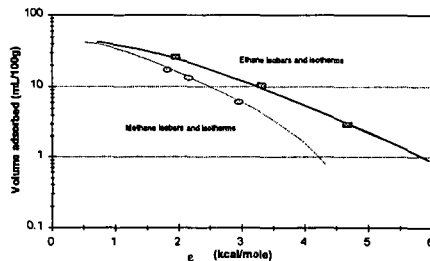


Figure 2
Comparison of Isotherms and Isobars
Methane and Ethane Adsorbed on PCB Carbon